Use of TPH Fractionation and Silica Gel Cleanup to Evaluate Risks to Groundwater from Petroleum Releases

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Objective

- Discuss Total Petroleum Hydrocarbon (TPH) methodology and regulatory criteria for groundwater sites
- Present TPH fractionation techniques
  - Massachusetts DEP (MA DEP) method
  - Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) method
- Discuss Silica Gel Cleanup (SGC) as a means to reduce bias in measuring TPH in groundwater
- Discuss preliminary data on fate and transport and risk to human health from petroleum metabolites
- Present findings from Navy field sites where TPH fractionation and SGC methods have been used to evaluate natural attenuation and risk-based closure options

TPH Background

- Many states use TPH to regulate groundwater quality at petroleum sites
  - Approximately 75% of states (TPHCWG, 1998)
- Persistent TPH detections in soil and groundwater prevent regulatory closure at many sites
  - Even when soluble hydrocarbons (e.g. BTEX) are absent or below criteria
- Elevated dissolved-phase TPH concentrations in the absence of soluble hydrocarbons can indicate sampling bias and lead to conservative remediation decisions

TPH Background (Continued)

- Application of TPH standards complicated because of variation in fate and transport and toxicity of petroleum constituents
- TPHCWG and MADEP methods overcome challenge by considering aliphatic and aromatic fractions separately
  - Aromatic and aliphatic groups divided into fractions based on equivalent carbon (EC) number
  - Screening criteria developed for different TPH fractions for soil and groundwater

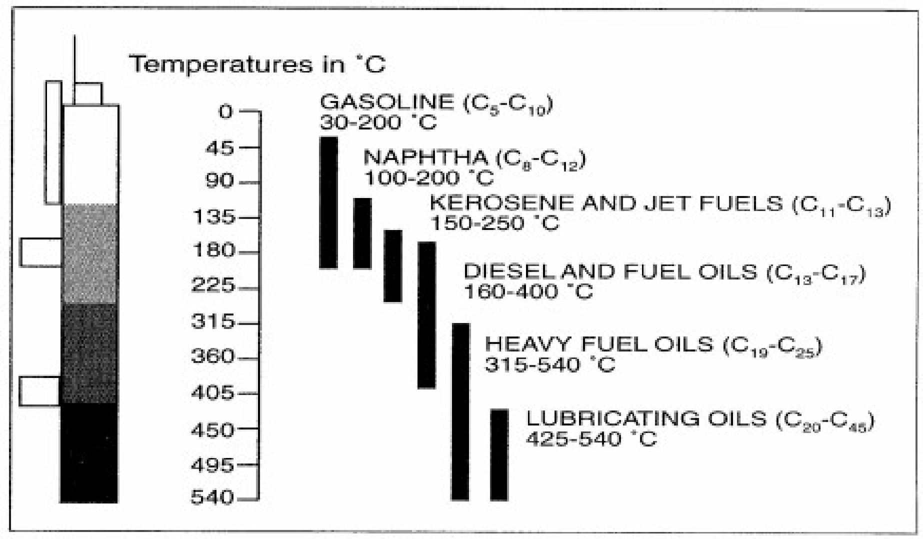
Dissolved Constituents in Petroleum Products

Compound Detected	Maximum Concentration in Groundwater (µg/L) in Equilibrium with:		
	Gasoline (1:1000)	Kerosene (1:10)	Diesel (1:10)
Benzene (C_6)	8,700	350	200
Toluene (C_7)	24,000	1,100	550
Ethylbenzene (C_8)	2,000	310	100
Xylenes (C_8)	3,800-8,600	380-660	170-230
Substituted Benzenes ($C_{9,10,11}$)	200-2,000	30-480	20-130
Naphthalene (C_{10})	990	640	170
Methyl Naphthalene (C_{11})	100-260	290-350	160-270
Acenaphthene (C_{12})	1	2	6
Fluorene (C_{13})	1	3	10
Phenanthrene (C_{14})	<1	<1	17
Anthracene (C_{14})	<1	12	25

Table modified from Zemo and Synowiec 1995

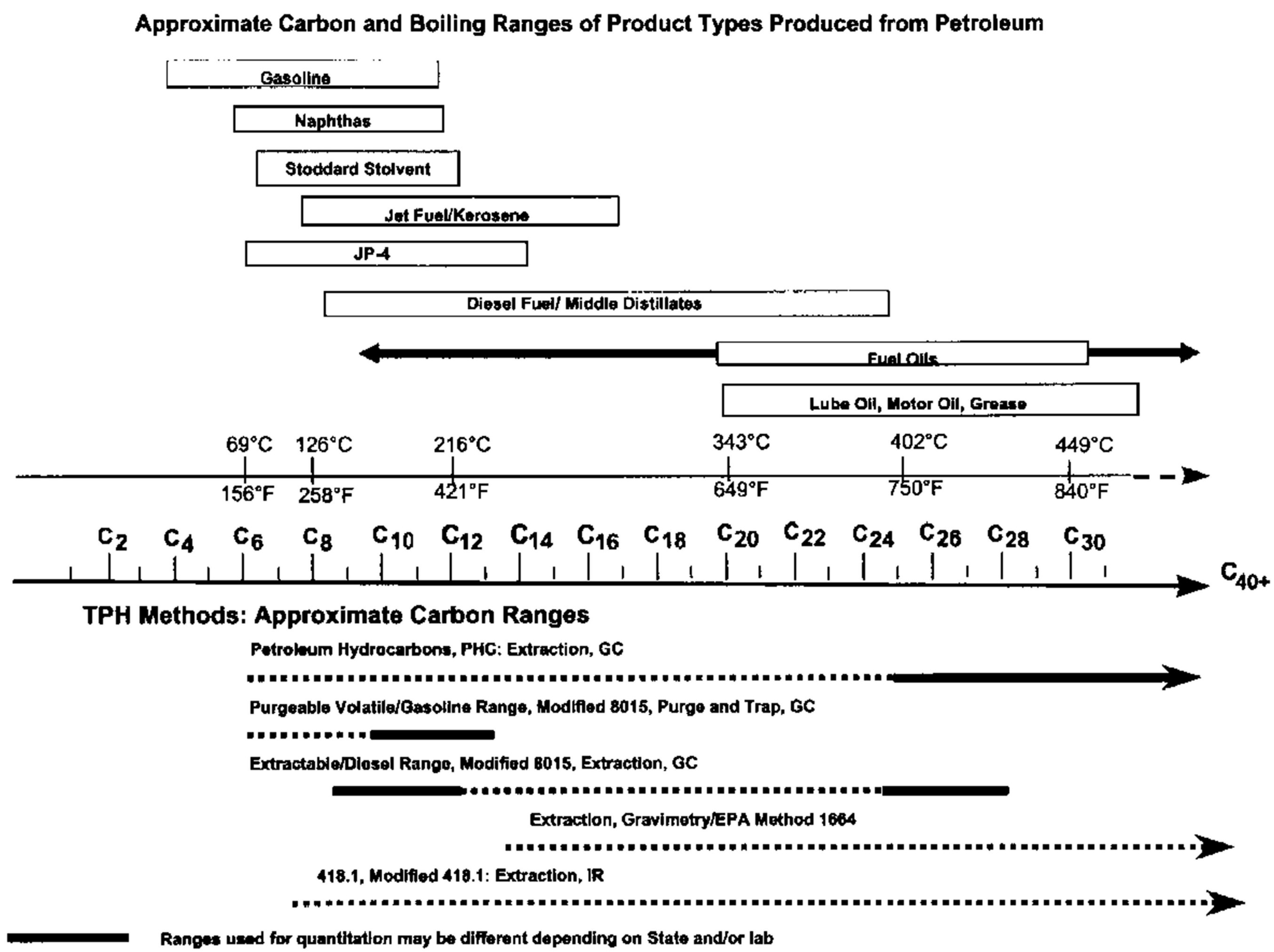
TPH Terminology

- Gasoline Range Organics (GRO)
  - TPHV, TPH-G
  - Volatile Petroleum Hydrocarbons (VPH)
  - C_5 to C_{12} hydrocarbons
  - Purge and trap or headspace analysis
  - Useful proxy for dissolved phase hydrocarbon constituents
  - MOGAS, AVGAS, stoddard solvent, mineral spirits
- Diesel Range Organics (DRO)
  - TPH-D
  - C_{10} to C_{28} hydrocarbons
  - Solvent extraction process
  - Extractable Petroleum Hydrocarbons (EPH)
  - Diesel, Jet Fuel, Kerosene
- Motor Oil, Bunker Fuel



Source: TPHCWG, 1998

TPH Terminology



Source: TPHCWG, 1998

TPH Analytical Methods

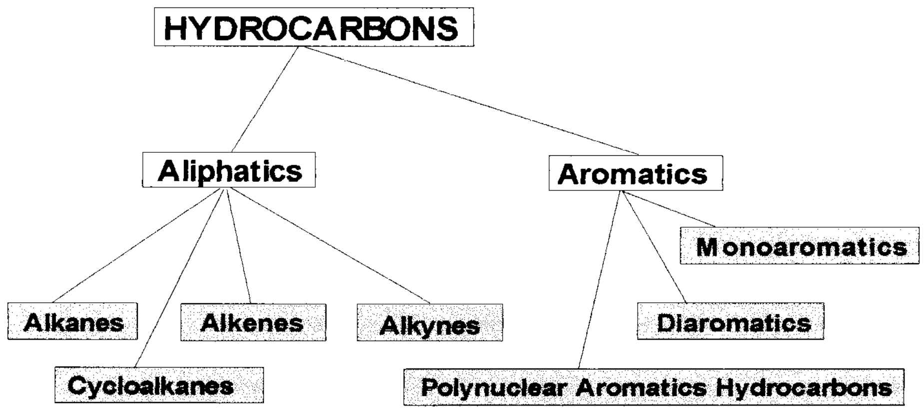
- **EPA Method 8015B**
  - Gas chromatography method quantifies volatile or semi-volatile hydrocarbon compounds within a selected boiling point/molecular weight range
  - Aggregate method
  - Purgeable and extractable petroleum fractions
  - Quantitation based on specific standard (e.g. diesel)
  - Typically does not include silica gel or other cleanup steps to remove polar compounds
  - TPH-GRO ~$25/sample; TPH-DRO ~$50/sample
- **EPA Method 418 Total Recoverable Petroleum Hydrocarbons**
  - Infrared spectroscopy
  - Sample extraction using Freon 113
  - Silica gel cleanup
  - Typically used as a screening method
  - ~$55/sample
- **EPA Methods 8260/8270 for individual constituents**

TPH Analytical Methods (Cont.)

- MA DEP TPH Fractionation
  - EPH - $85
  - VPH - $54
- TPHCWG TPH Fractionation
  - $295/sample

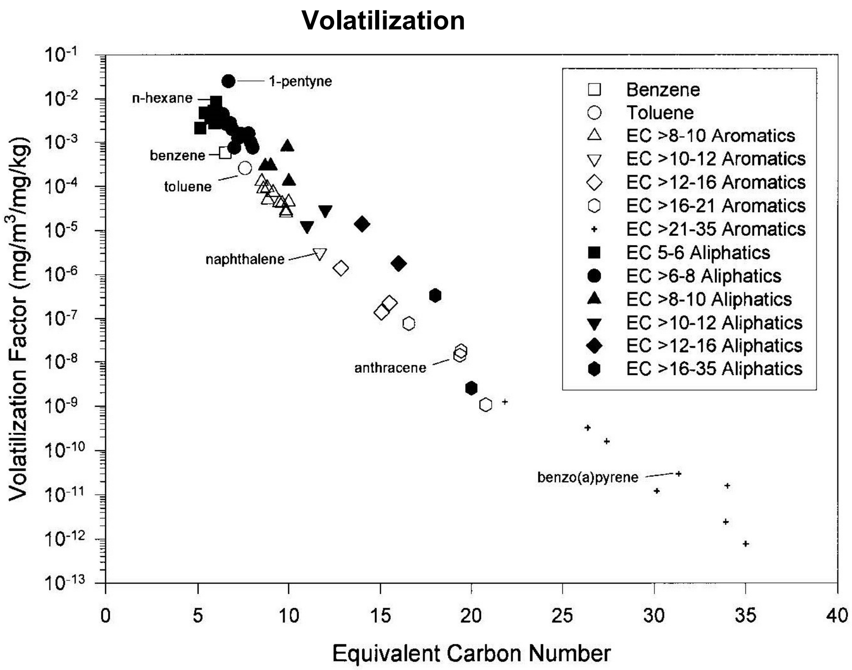
TPH Fractionation Methods

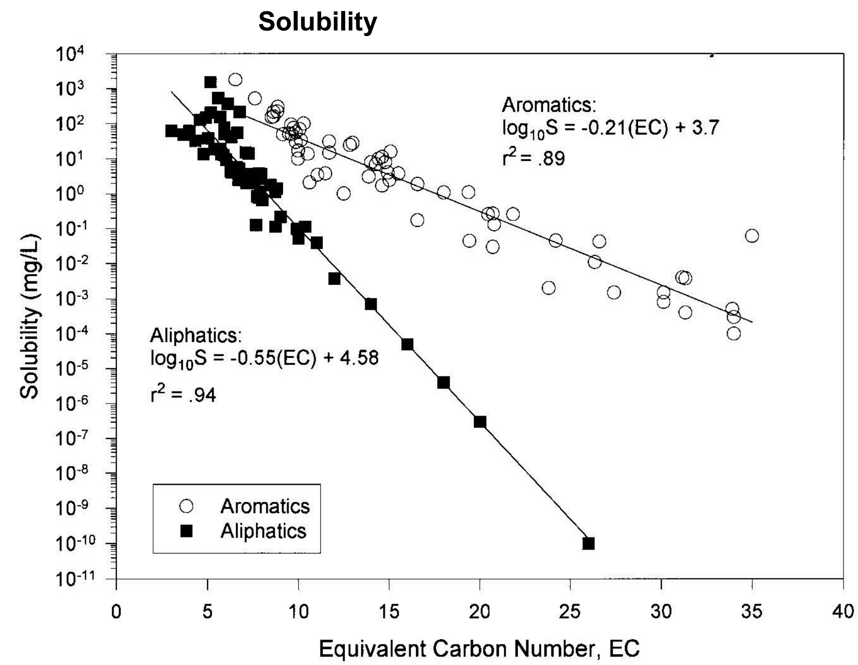
- First divide petroleum constituents into aliphatic and aromatic fractions
- Subdivide according to chemical class, boiling point ranges
- MA DEP Method
  - Fractions based on expected toxicity of individual constituents
- TPHCWG Method
  - Fractions based on environmental behavior of individual constituents
- Petroleum fractions used to evaluate non-cancer risk
- Cancer risk evaluated based on individual petroleum constituents



Source: TPHCWG, 1998

Fate and Transport Properties





Source: TPHCWG, 1998

- **Hydrocarbons with similar boiling point ranges behave similarly in the environment**
- **Volatilization and solubility show a similar relationship with equivalent carbon (EC) number – increasing hydrophobicity with increasing EC number**

TPH Fractions – TPHCWG Method

- Complex mixtures make risk assessment difficult
- Data unavailable for many individuals components of petroleum hydrocarbons
- Weathering and natural attenuation impact nature of complex mixtures (e.g. dissolution, volatilization)
- Reasonable to assume components with similar boiling points and chemical structure behave similarly in environment

Hydrocarbon Fractions Defined by the Total Petroleum Hydrocarbon Criteria Working Group

Range of Equivalent Carbon Number (EC)	Avg EC	Classification
C_5-C_7	6.5	Aromatic
>C_7-C_8	7.5	Aromatic
>C_8-C_{10}	9.0	Aromatic
>C_{10}-C_{12}	11	Aromatic
>C_{12}-C_{16}	14	Aromatic
>C_{16}-C_{21}	18.5	Aromatic
>C_{21}-C_{35}	28.5	Aromatic
C_5-C_6	5.5	Aliphatic
>C_6-C_8	7.0	Aliphatic
>C_8-C_{10}	9.0	Aliphatic
>C_{10}- C_{12}	11	Aliphatic
>C_{12}- C_{16}	14	Aliphatic
>C_{16}- C_{21}	18.5	Aliphatic

Source: TPHCWG, 1998

TPH Fraction Screening Criteria

- Risk-based screening levels (RBSLs) developed for soil and groundwater
- Residential and industrial land use setting
- Screening models assume linear partitioning behavior (e.g. soil, vapor, moisture)
- RfDs and RfCs developed by TPHCWG
- Addresses only human health risks

Example RBSLs (TPHCWG)

Table 3. Pathway-specific Soil RBSLs for TPHCWG Petroleum Fractions[a]

Equivalent Carbon Number Range	C_{sat} (mg/kg)	Leaching To Groundwater (mg/kg)	Volatilization to Outdoor Air (mg/kg)	Direct Contact with Surface Soil[b] (mg/kg)
Aliphatics				
>5–6	470	$>C_{sat}$	$>C_{sat}$	200,000
>6–8	260	$>C_{sat}$	$>C_{sat}$	200,000
>8–10	140	$>C_{sat}$	$>C_{sat}$	4,000
>10–12	86	$>C_{sat}$	$>C_{sat}$	4,000
>12–16	38	$>C_{sat}$	$>C_{sat}$	4,000
>16–21	16	$>C_{sat}$	$>C_{sat}$	90,000
Aromatics				
>5–7[c]	1,600	1	10	100
>7–8	1,300	200	$>C_{sat}$	9,000
>8–10	1,000	300	$>C_{sat}$	2,000
>10–12	630	500	$>C_{sat}$	2,000
>12–16	290	$>C_{sat}$	$>C_{sat}$	2,000
>16–21	100	$>C_{sat}$	$>C_{sat}$	1,000
>21–35	8.3	$>C_{sat}$	$>C_{sat}$	1,000

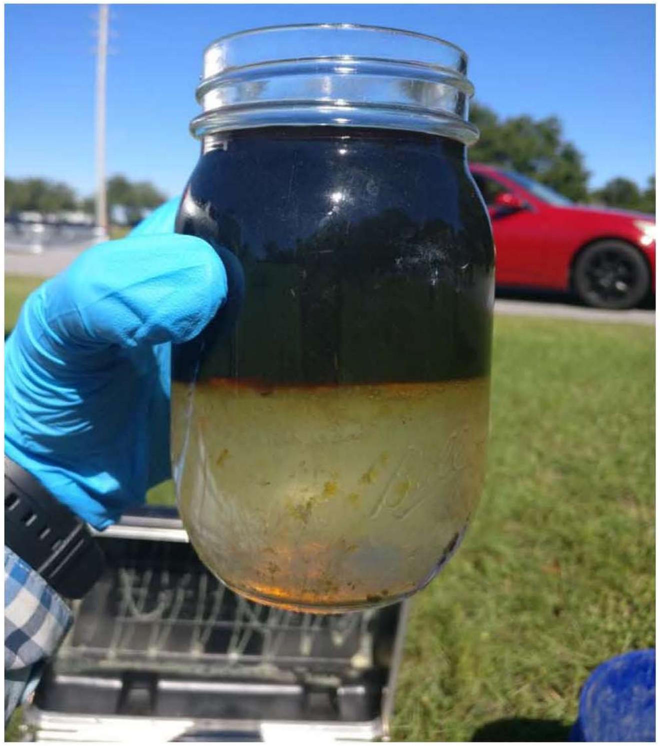
Notes:
[a] All RBSLs are based on residential exposure scenarios.
[b] The "direct contact with surface soil" exposure pathway combines four exposure pathways: soil ingestion, dermal exposure to soil, and inhalation of soil vapor and fugitive dust.
[c] $EC_{>5}$–EC_7 aromatic fraction RBSLs are calculated using provisional toxicity criteria (US EPA 1998).
"$>C_{sat}$"—substituted for pathway RBSLs that exceed C_{sat} for a given fraction.

Source: TPHCWG, 1998

UST 25, NAS Pensacola

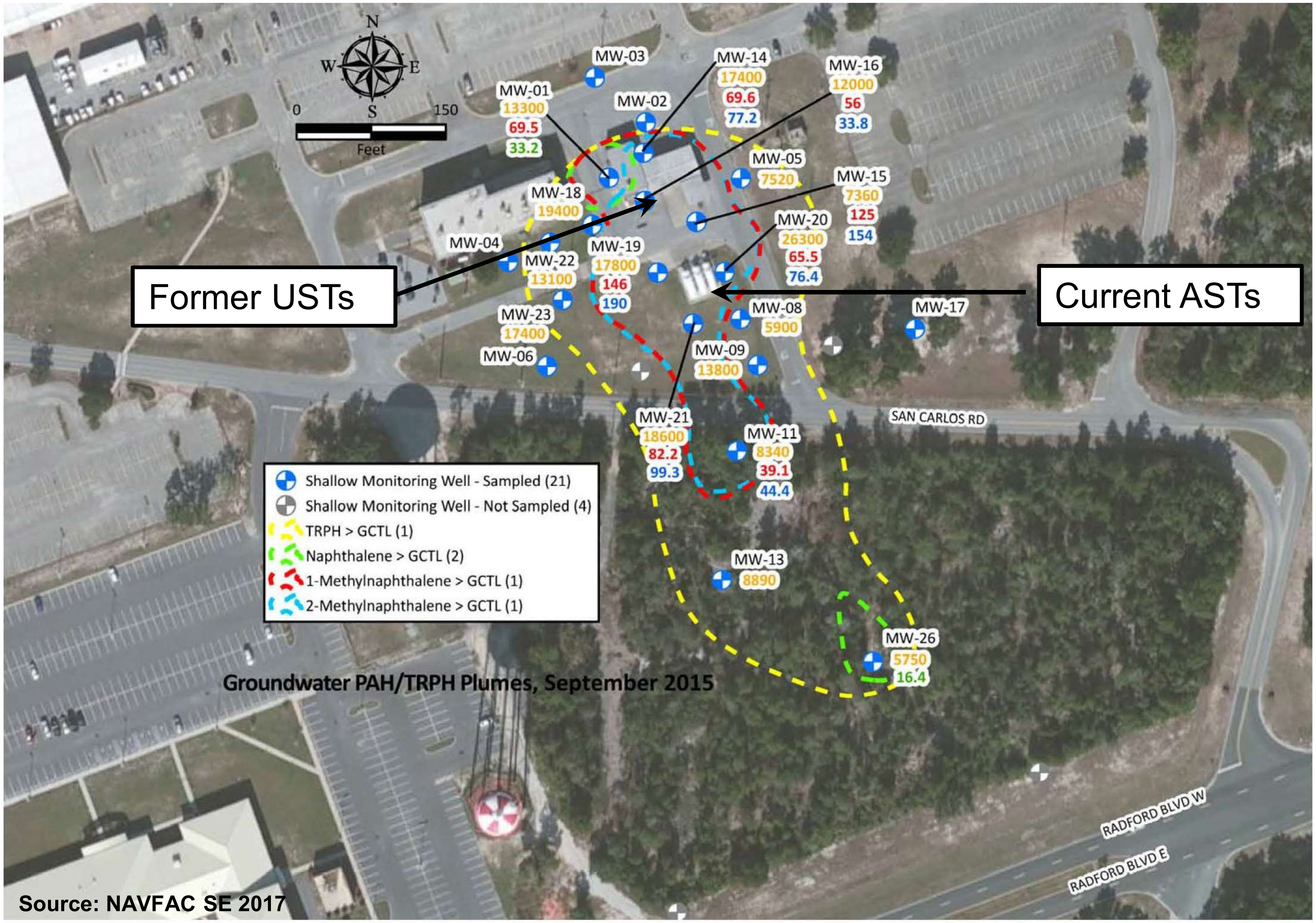
- Bldg. 1932 Navy Exchange "Touch N Go" Service Station
- Bldg. 1932 constructed in 1959 and contained two vehicle service areas
- Former USTs for diesel and gasoline
- 500-gal waste oil UST (removed in 1994)
- Site assessment in 2000 indicated free product (>1 ft) and naphthalene and BTEX exceeding groundwater criteria
- Currently only TPH, naphthalene, and methylnaphthalene(s) exceed groundwater criteria

Weather Product – UST 25

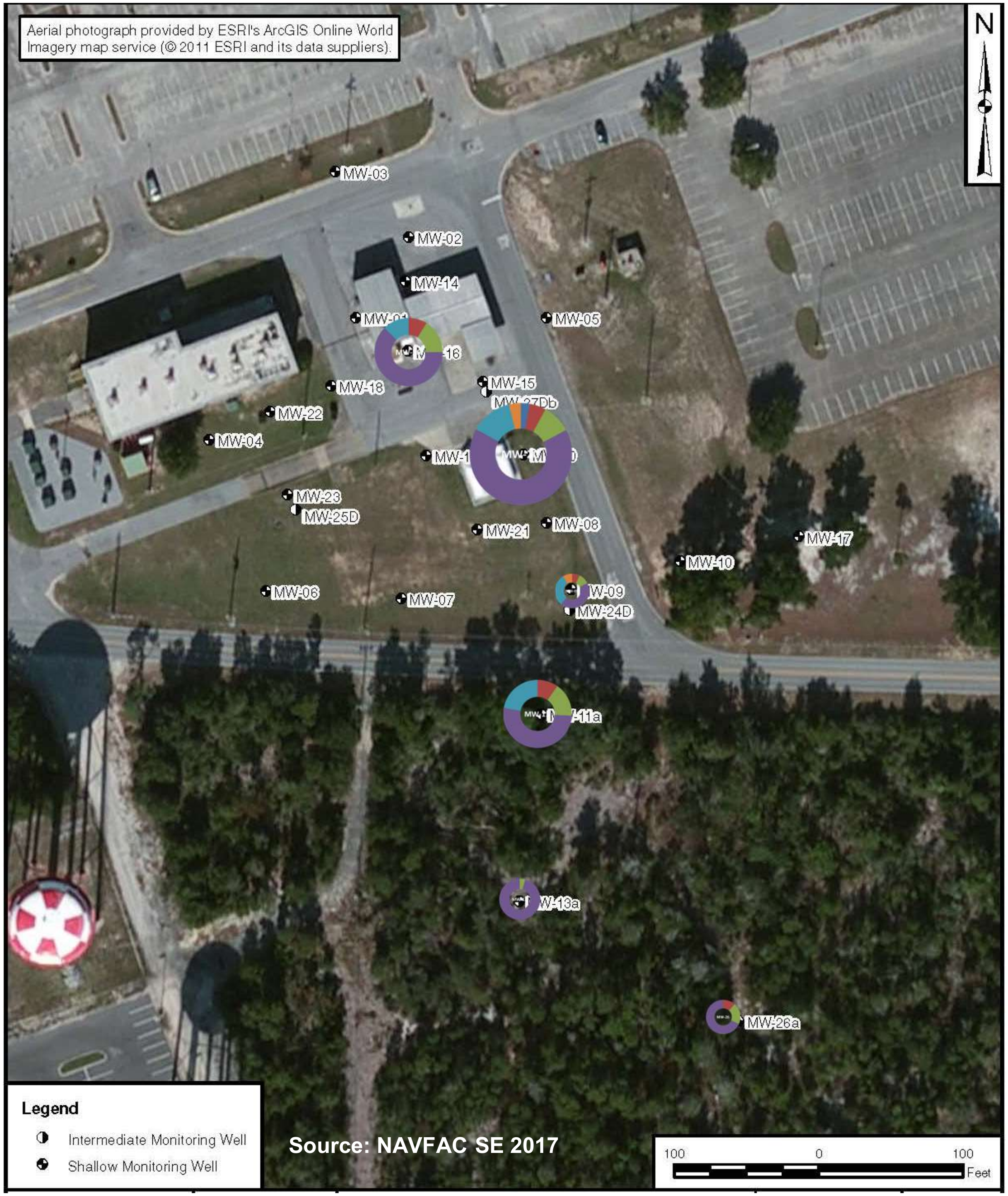


Source: NAVFAC SE 2017

NAS Pensacola, UST 25

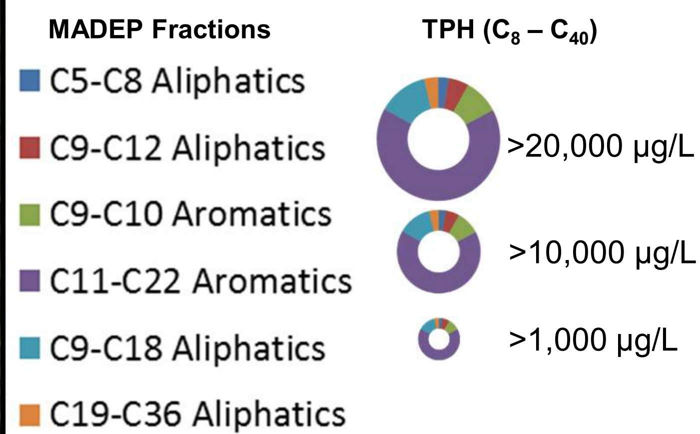


Source: NAVFAC SE 2017

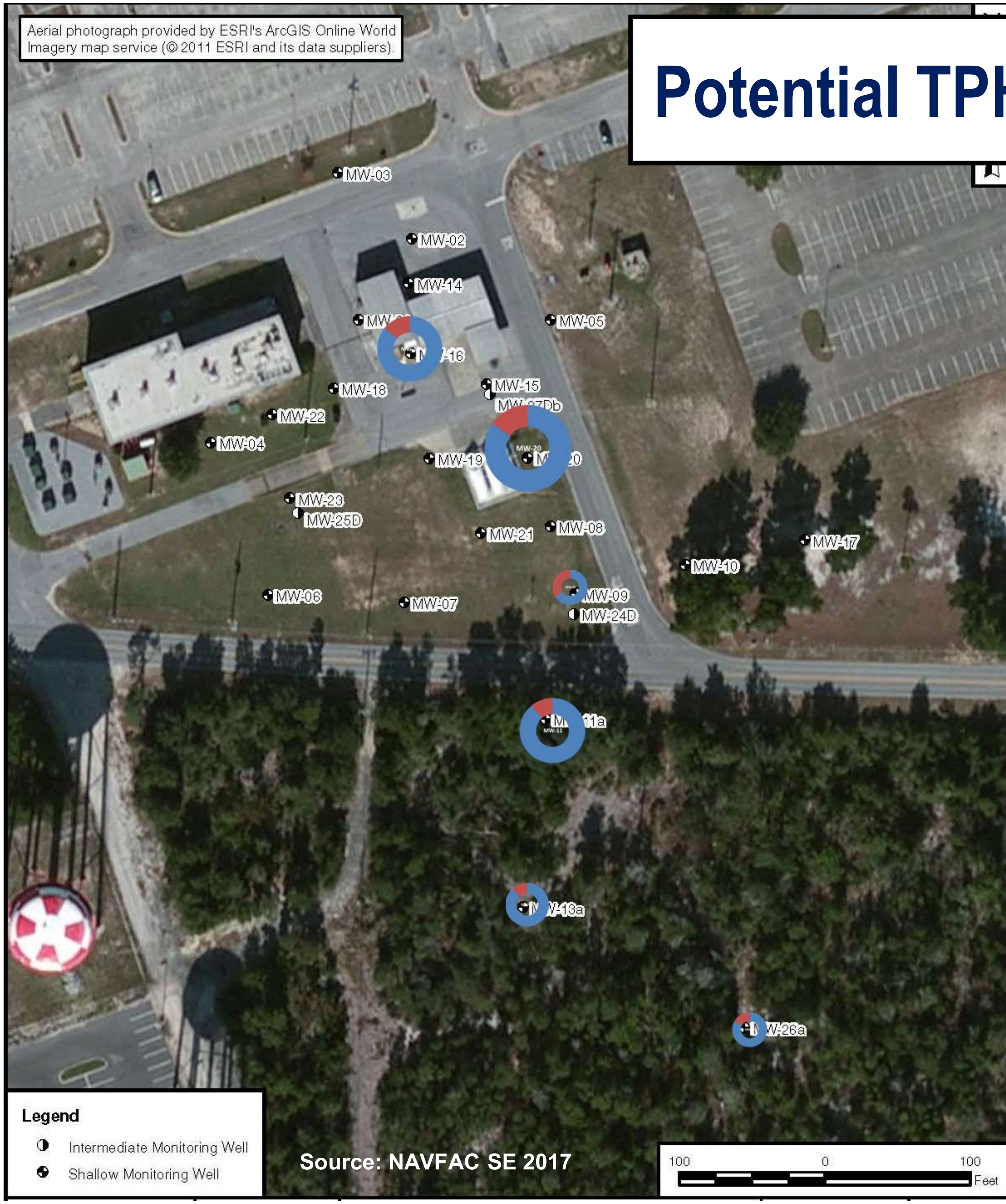


TPH Fractions

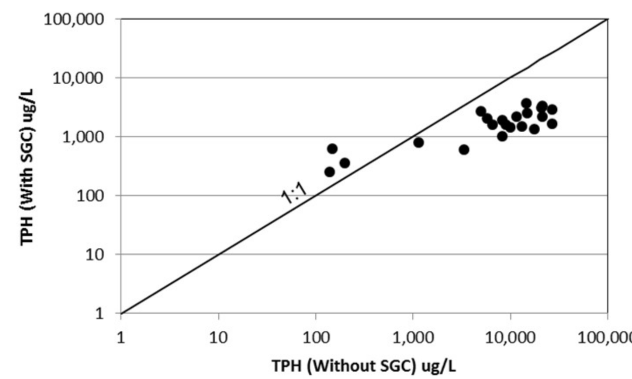
- Most significant fraction C_{11} – C_{22} aromatics (e.g. methyl naphthalenes)
- C_{11}-C_{22} >50% of total in most wells
- Consistent with dissolved phase constituents
- Persistent higher molecular weight fractions (lower biodegradation rates)



Potential TPH Interference?



- Silica Gel Cleanup (SGC) step to remove polar compounds
- SGC reveals presence of polar compounds



TPH ($C_8 – C_{40}$)

>20,000 µg/L

>10,000 µg/L

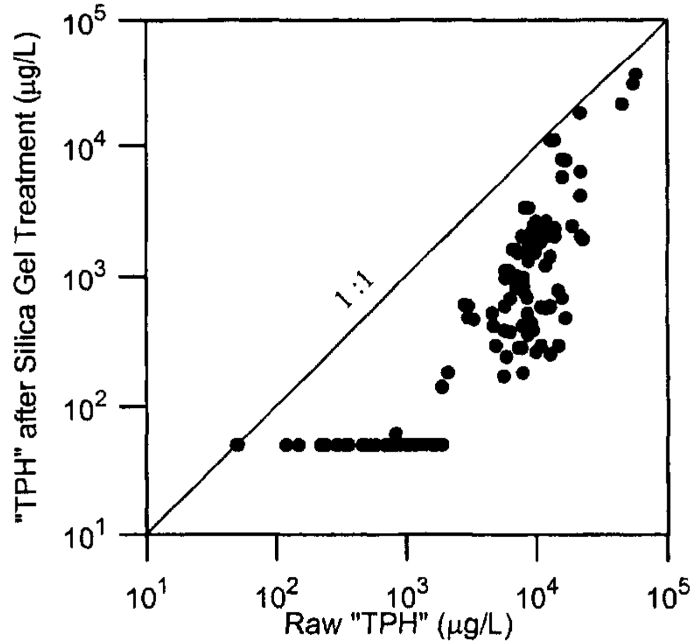
>1,000 µg/L

% TPH

% Polar Compounds

Sources of TPH Interference

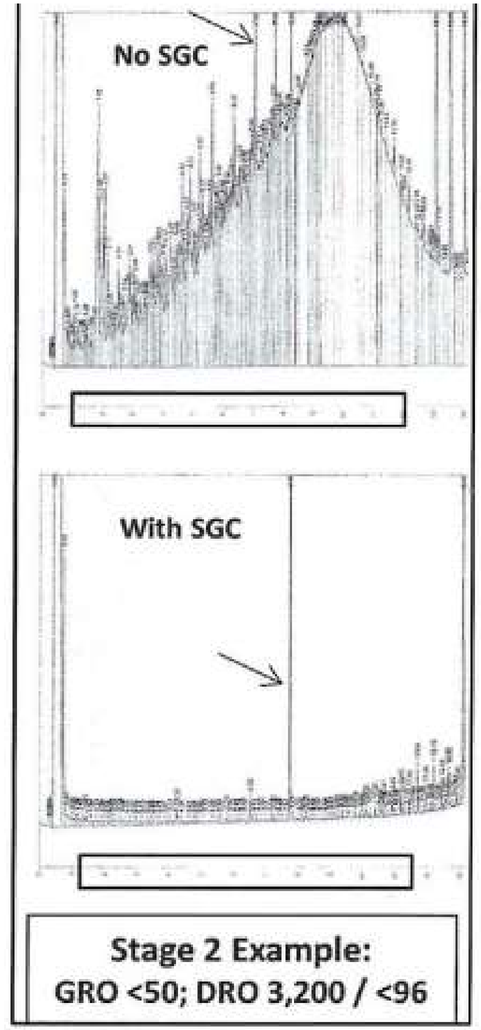
- **Sampling groundwater from smear zones can lead to positive bias**
  - **Non-dissolved petroleum (e.g. sheens)**
  - **Petroleum sorbed on sediment in turbid samples**
  - **Polar compounds and petroleum metabolites**
- **Field and laboratory methods to minimize bias**
  - **Well re-development**
  - **Low-flow sampling, passive diffusion**
  - **Filtration**
  - **Gravity separation**
  - **Silica gel cleanup (SGC)**



Source: Lundegard and Knott 2001

Polar Metabolites

- Petroleum releases consist of complex mixtures of many chemicals
- Most compounds are hydrocarbons (containing C,H)
- Crude oils contain significant amounts of polar organic molecules (N, S, O)
- Refined products may contain additives
- Weathered releases contain partially oxidized polar metabolites (i.e. more water soluble)
  - Alcohols
  - Phenols
  - Ketones
  - Aldehydes
  - Organic acids

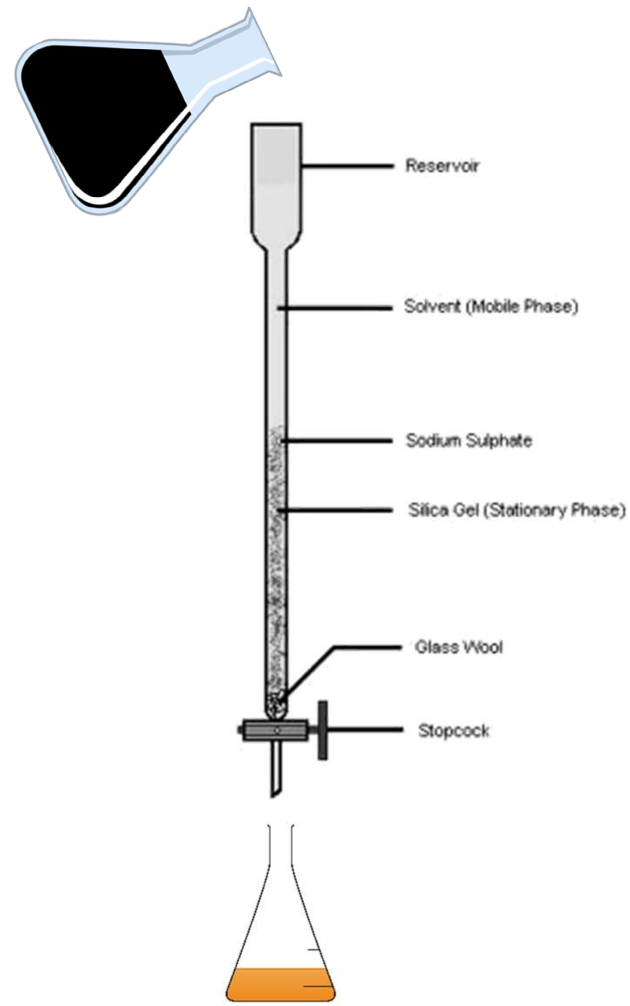


Concentration in µg/L

Source: Zemo et al. 2016

Silica Gel Cleanup

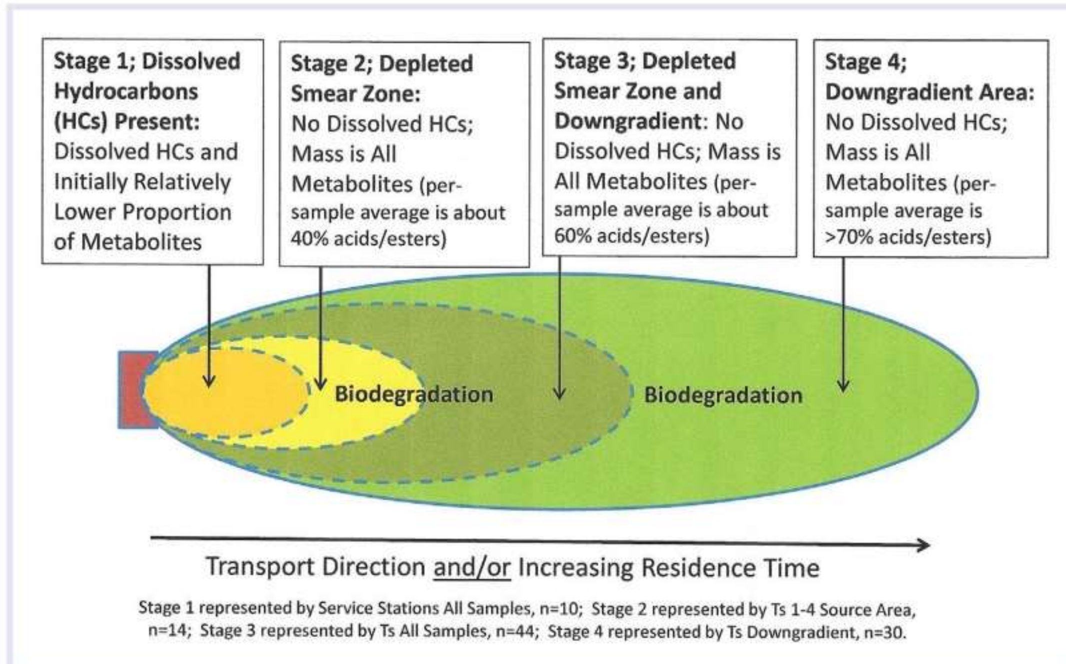
- Analysis of complex petroleum mixtures by gas chromatography often results in co-elution of compounds due to similar boiling points
- Unresolved compounds result in "hump" on chromatogram, referred to a "unresolved complex mixture" or UCM
- UCMs may contain 60,000 - 250,000 individual compounds
- Weathering (including biodegradation and photo-oxidation) can further increase complexity of UCMs
- SGC (USEPA Method 3630) used to separate compounds of differing polarity
- Not applicable to volatile fraction (GRO)
- SW-846 Method 3630C ~$45/sample



Source: NAVFAC 2017

Life Cycle of TPH Plume

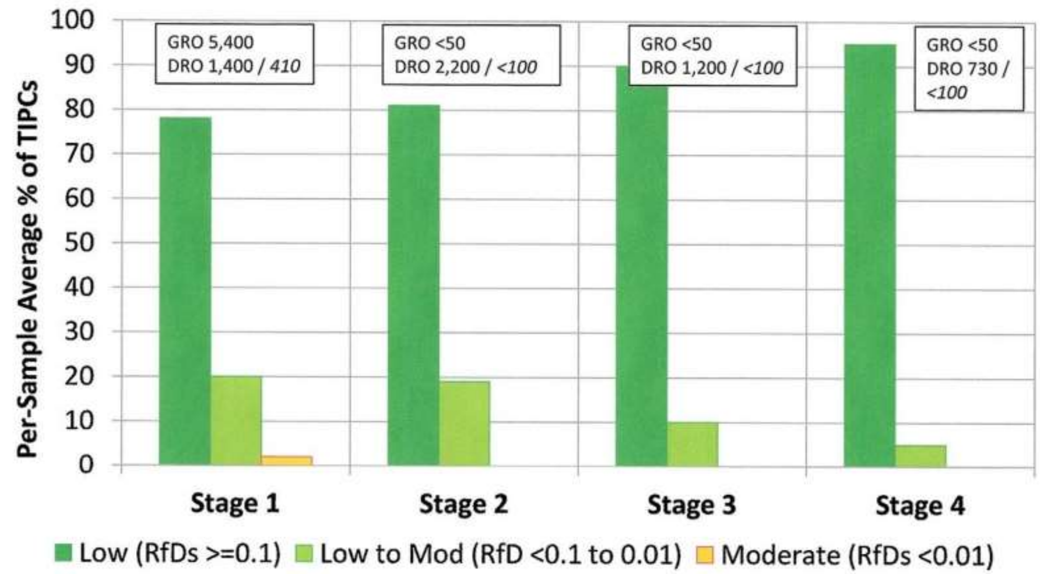
- Near source zone dissolved hydrocarbons (e.g. TPH-DRO) typically present with lower proportion of petroleum metabolites
- Downgradient plume contains less dissolved hydrocarbon mass and higher proportion of metabolites (e.g. >80% petroleum metabolites)
- Distal plumes may comprised completely of petroleum metabolites and may not be representative of TPH



Source: Zemo et al. 2016

Risk Evaluation of TPH Plumes

- Majority of metabolites exhibit low toxicity to human receptors
- Continued biodegradation of metabolites results in increasingly lower human toxicity profile
- Ecological risks considered when groundwater discharges to surface water receptors
- Limited studies on potential ecological receptors
- Hyporheic zone expected to provide attenuation of petroleum metabolites

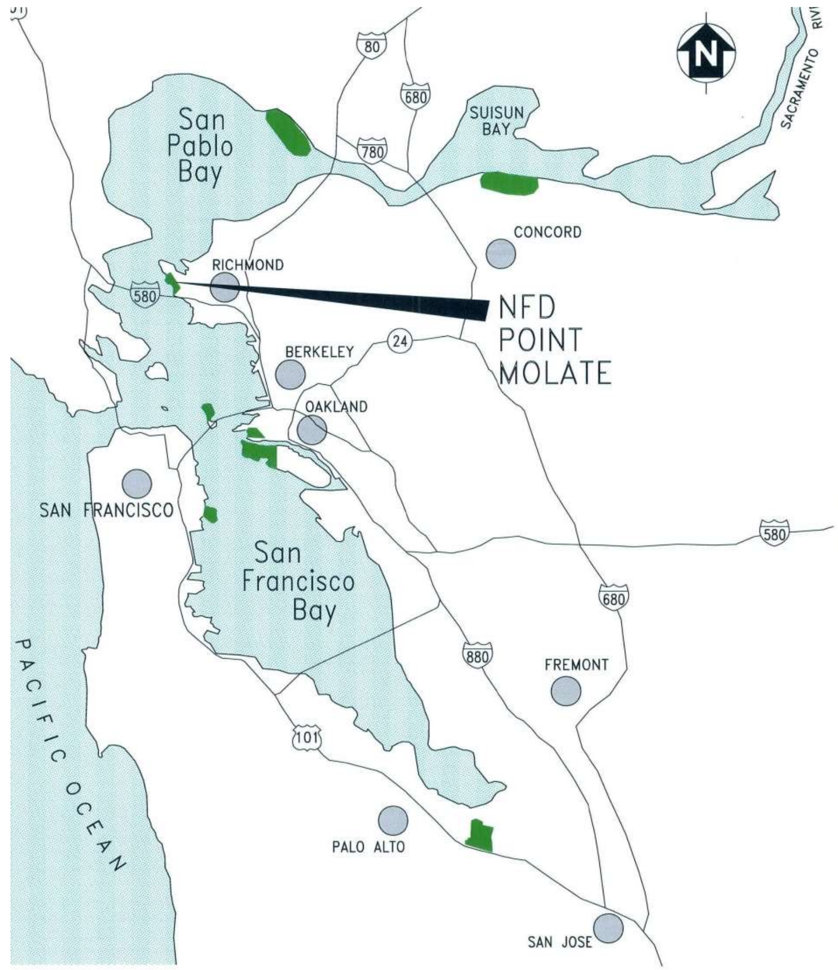


TIPCs = tentatively identified polar compounds (metabolites only). GRO concentration and DRO concentration without/*with* SGC (ug/L) is the average for the population representing the stage. Results are for upland samples without entrained product collected 2011 – 1Q2015. 2,4- and 3,5- DTBP are classified as alkylphenols, but are assigned low toxicity ranking based on toxicity data for the di-substituted alkylphenol category from USEPA (2009).

Source: Zemo et al. 2016

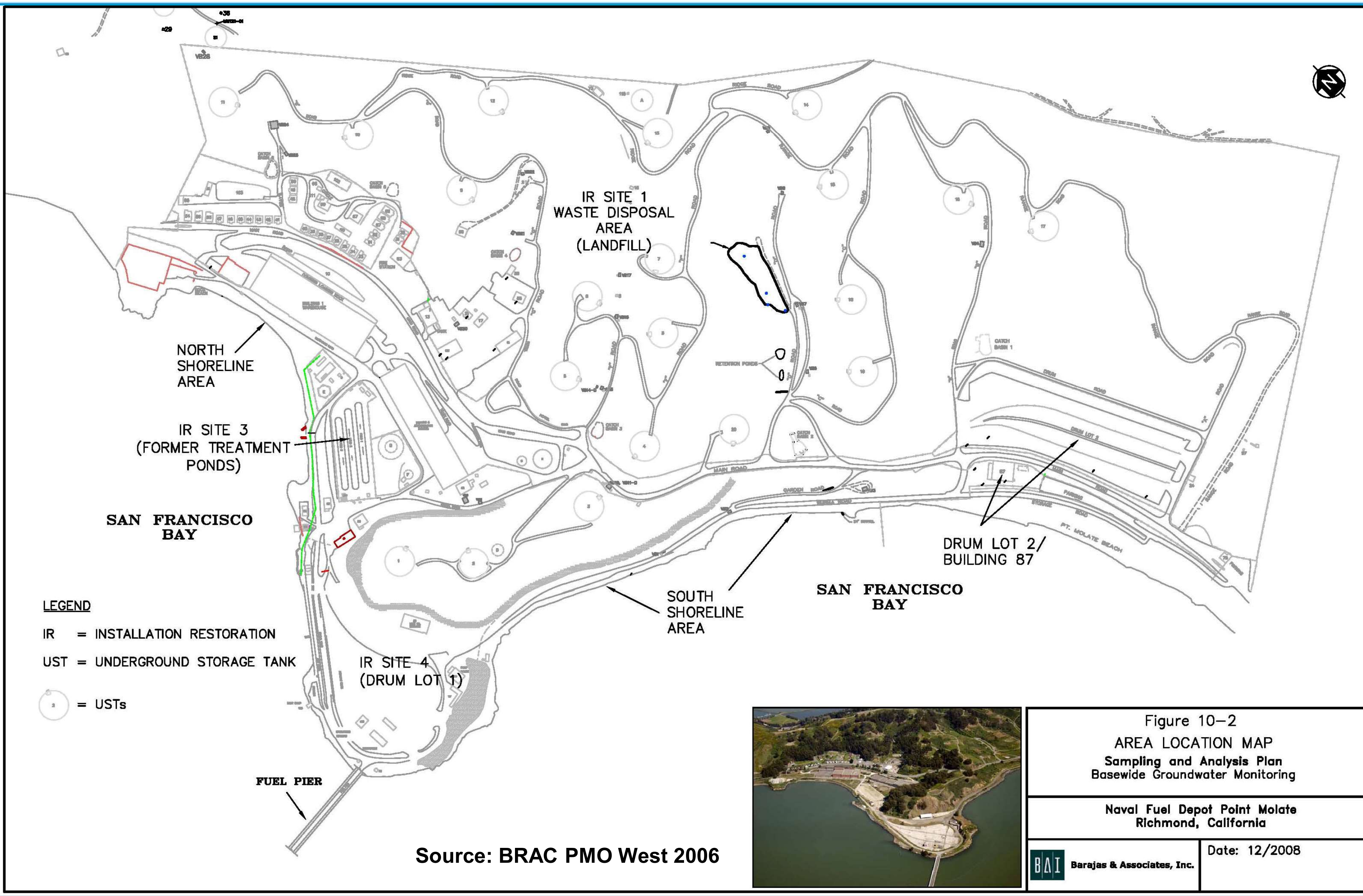
Naval Fuel Depot (NFD) Point Molate

- Operated from 1942 to 1998 as a bulk storage and transfer facility
- Twenty 2-MG USTs along with smaller USTs
- Fuel releases through valve leakage and tank overfills
- Fuels included diesel, JP-5, motor oil, and bunker fuel
- BRAC 1995
- October 2003 Navy transferred 85% of property to City of Richmond
- Groundwater monitoring includes TPH by US EPA 8015M using both standard and silica gel cleanup and lab filtration to minimize interference from polar compounds



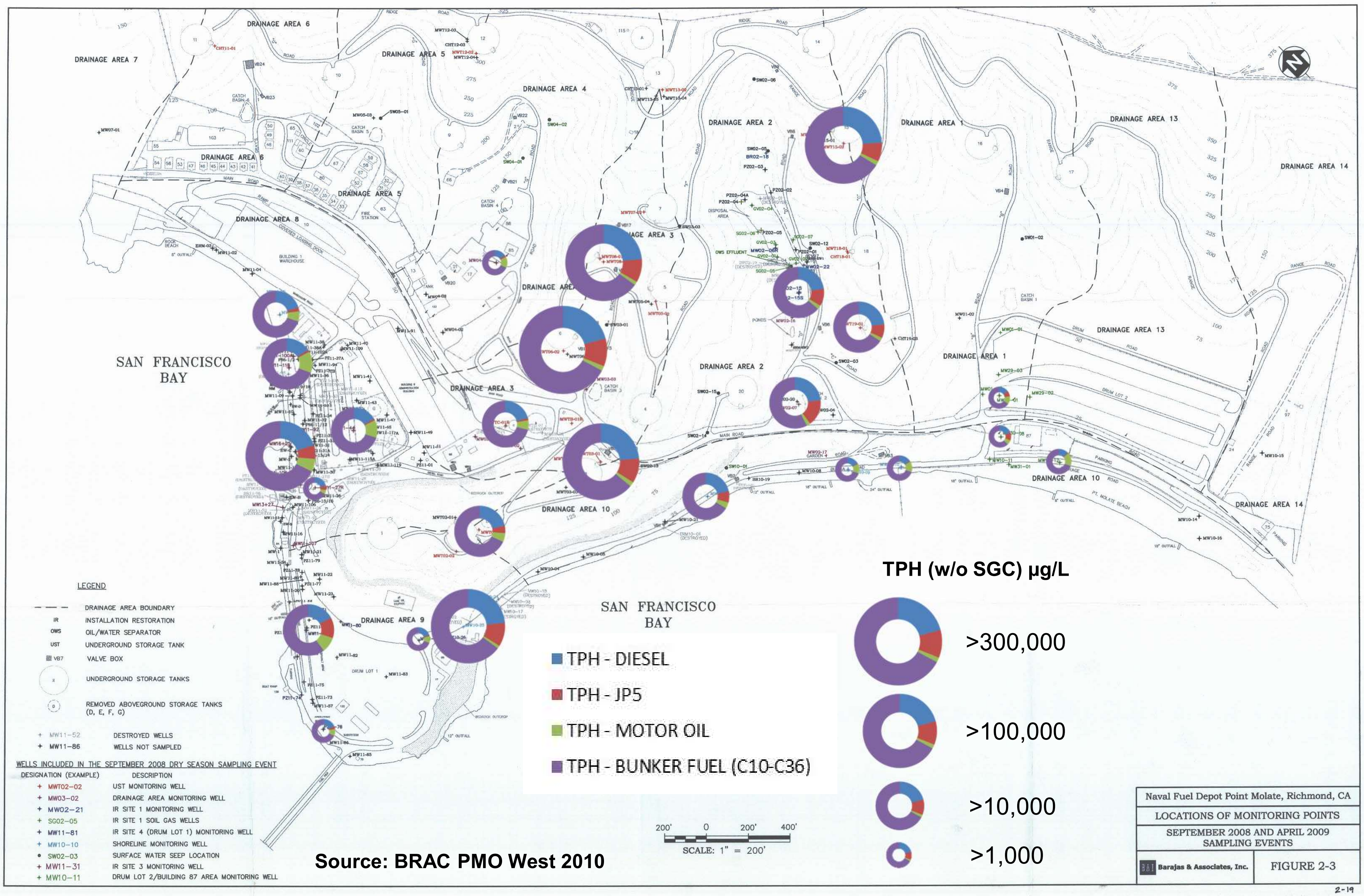
Source: BRAC PMO West 2008

NFD Point Molate



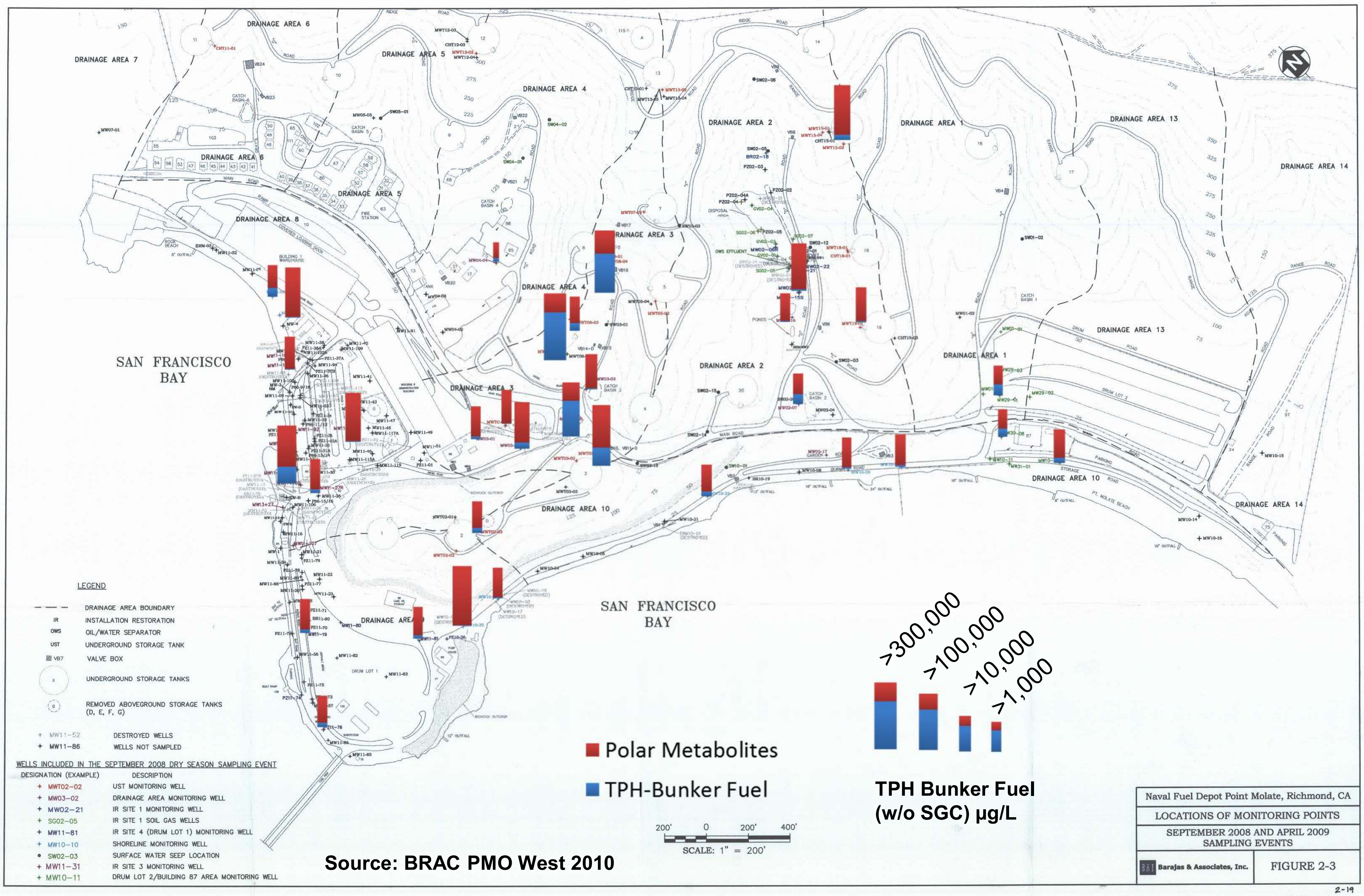
Source: BRAC PMO West 2006

TPH Distribution



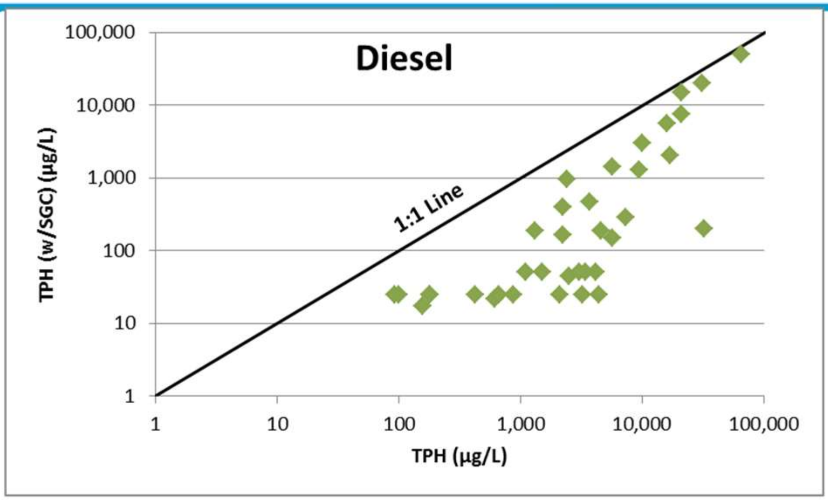
Source: BRAC PMO West 2010

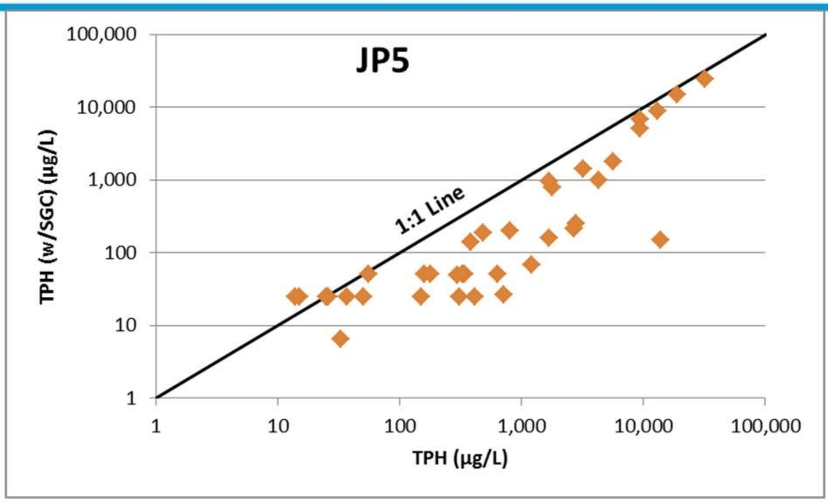
Petroleum Metabolite Distribution

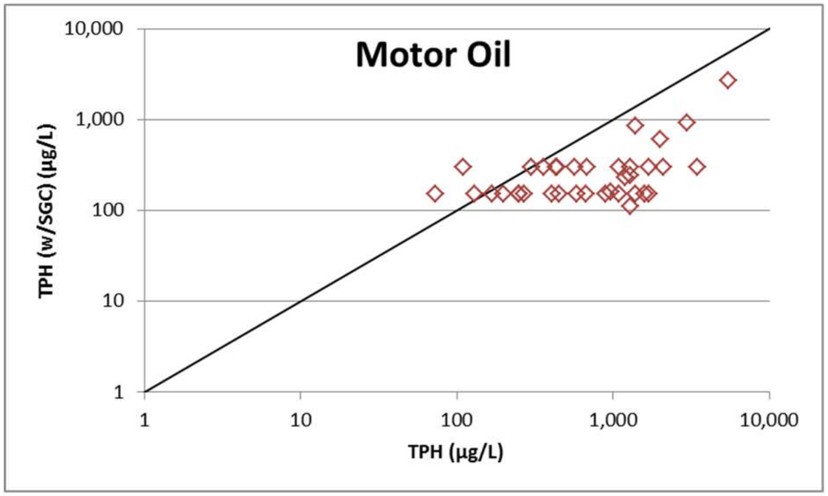


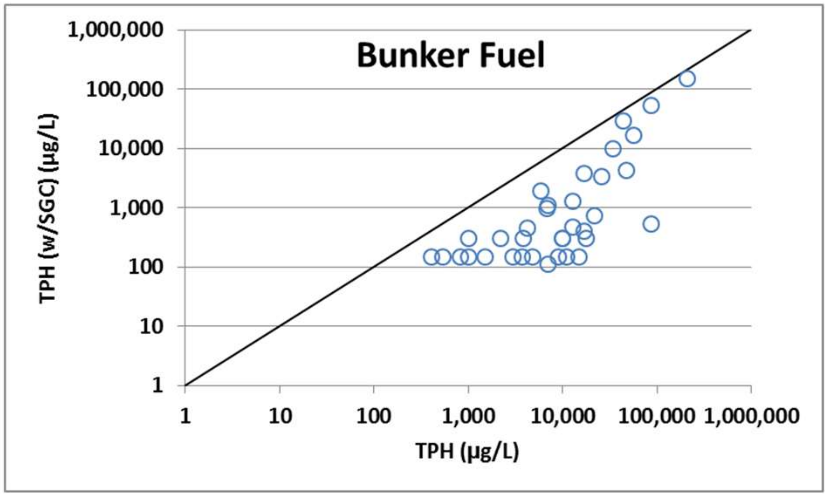
Source: BRAC PMO West 2010

Consistent Bias in TPH Analysis





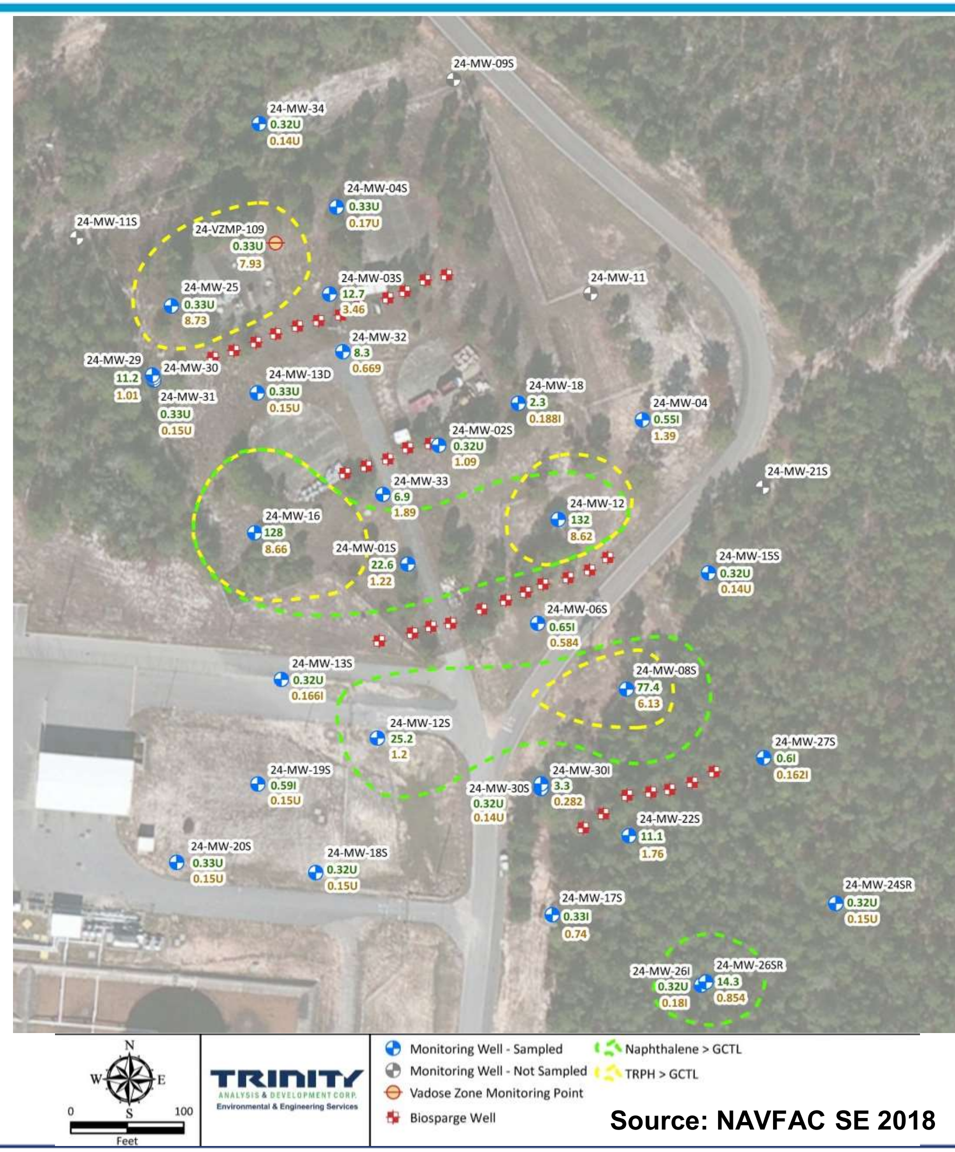




- **Non-dissolved Bias in TPH analysis**
- **Sampling groundwater from smear zones can lead to positive bias**

NAS Pensacola, UST 24

- Sherman Field Tank Farm
- Operated from 1945 to 1995
- Four former USTs/14,000 barrel capacity
- JP-4
- Historic product thickness greater than 1 ft
- BTEX, TPH constituents in groundwater
- Current remedy includes biosparging for dissolved-phase plume and MNA

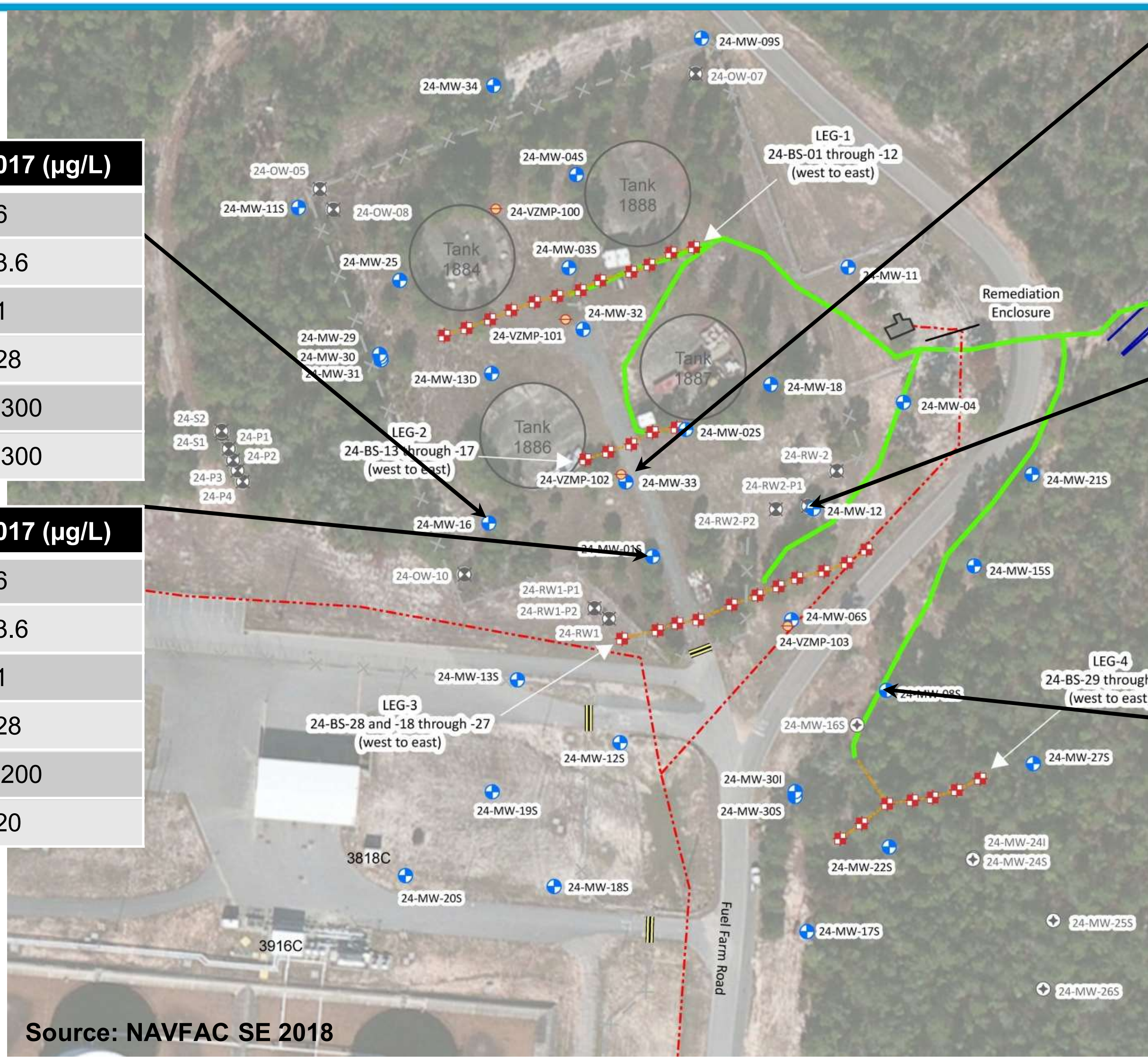


Source: NAVFAC SE 2018

TPH Distribution

Parameter	2017 (µg/L)
1-MN	36
2-MN	43.6
Benzene	11
Naphthalene	128
TPH	7,300
TPH (w/SGC)	1,300

Parameter	2017 (µg/L)
1-MN	36
2-MN	43.6
Benzene	11
Naphthalene	128
TPH	2,200
TPH (w/SGC)	520



Parameter	2017 (µg/L)
1-MN	*ND*
2-MN	*ND*
Benzene	0.41
Naphthalene	*ND*
TPH	1,500
TPH (w/SGC)	600

Parameter	2017 (µg/L)
1-MN	47.8
2-MN	60.6
Benzene	6.2
Naphthalene	132
TPH	2,500
TPH (w/SGC)	1,300

Parameter	2017 (µg/L)
1-MN	21.6
2-MN	22
Benzene	13.2
Naphthalene	77.4
TPH	9,000
TPH (w/SGC)	2100

Summary

- Persistent TPH detections in soil and groundwater prevent regulatory closure at many sites
  - –Even when soluble hydrocarbons (e.g. BTEX) are absent
- TPHCWG and MADEP fractionation methods can refine remediation goals by evaluating risks associated with individual petroleum fractions
  - Document weathering and natural attenuation
  - Apply fraction-specific cleanup criteria for soil and groundwater
- Sampling groundwater from smear zones can result in significant positive bias for TPH
- Weathered petroleum releases contain partially oxidized compounds that are more polar than hydrocarbons (i.e. more water soluble)
  - Metabolites including alcohols, phenols, ketones, aldehydes, and organic acids

Summary

- Laboratory silica gel cleanup (SGC) can implemented to remove polar compounds (including biodegradation metabolites)
- Studies on the human health risks with polar metabolites indicate relatively low risks
- Continued biodegradation of metabolites results in increasingly lower human toxicity profile
- Limited studies done on potential ecological receptors
    - Groundwater discharges to surface water receptors
    - Attenuation in hyporheic zone sediments

Knowledge Check

- When would TPH fractionation and silica gel cleanup techniques be appropriate to use on petroleum sites?
  - Heavily weathered sites
  - Higher risk, lighter petroleum fractions have attenuated (e.g. BTEX) below regulatory concern
  - Heavier-end refined products (e.g. hydraulic oils, mineral oil, lube oil, NSFO)
  - Sites approaching regulatory closure with only TPH exceeding criteria

Contacts and Questions

Points of Contact
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Questions ?